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An Acyclic Arsenium Cation Stabilised by a Single P-As π-Interaction and a Cyclic Diphosphinophosphonium Salt

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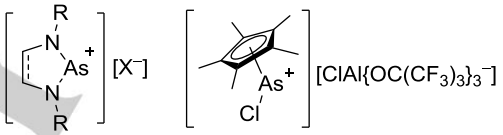
Dedication ((optional))

Abstract: Stable acyclic arsenium cations R_2As^+, isoelectronic analogues of germylenes, are rare in comparison to the corresponding phosphenium cations. The first example of a diphosphaarsenium salt $[\{(Dipp)_2P\}_2As][Al\{OC(CF_3)_3\}_4].1½PhMe$ (**2**) is described. This salt exhibits remarkable stability due to delocalisation of a lone pair from a planar phosphorus centre into the vacant p-orbital at arsenic; the bonding in **2** has been probed using DFT calculations. An attempt to synthesise an analogous diphosphaphosphenium salt unexpectedly generated the cyclic phosphonium salt [*cyclo*-$\{(Mes)P\}_2P(Mes)_2][BAr^F_4]$.CyMe (**5.CyMe**), via cyclisation of a putative phosphine-substituted diphosphene cation intermediate.

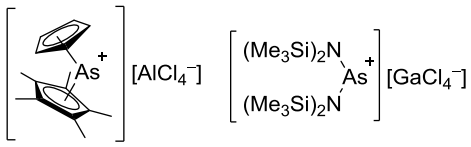
Since the discovery of the first two-coordinate phosphorus cation over 50 years ago, there has been continued interest in these species and their heavier congeners, both as isolated cations and as ligands to transition metals.[1-3] A significant underlying reason for this is the isoelectronic relationship between pnictenium cations R_2E^+ (E = P, As, Sb, Bi) and the corresponding tetrylenes R_2E (E = Si, Ge, Sn, Pb). Like singlet tetrylenes, pnictenium cations possess a lone pair and a vacant p-orbital at the pnictogen centre. This confers both electrophilic and nucleophilic character on pnictenium cations, although the positive charge at the pnictogen centre renders these compounds substantially less nucleophilic and more electrophilic than their tetrylene analogues, making them poor σ-donors, but good π-acceptor ligands.

Arsenium cations are less numerous than their phosphorus analogues and the vast majority of isolated two-coordinate arsenium ions are cyclic, *N*-substituted species (**I**),[4] analogues of *N*-heterocyclic carbenes. By comparison, structurally characterised acyclic arsenium ions are limited to just a few examples. The formally two-coordinate arsacenium cation **II** was reported in 1983 by Jutzi and co-workers,[5] while Krossing and co-workers subsequently reported the chloroarsacenium cation **III**.[6] The poorly stable diaminoarsenium cation **IV** was reported by Shulz and co-workers[7a] and these authors have very recently isolated the room temperature-stable diaminoarsenium salts $[(Mes*NH)_2As][X]$ (**V**) [X = AsF_6, BF_4, $AlCl_4$, $GaCl_4$].[7b] In addition, a very small number of related acyclic stibenium and bismuthenium cations have been reported.[8]

It is notable that, while three-coordinate, electron-precise arsino-phosphonium cations of the form $[R_2As\text{-}PR_3]^+$ are known,[9] no examples of two-coordinate phosphorus-substituted arsenium cations have been reported to date.[10] The diaminoarsenium cations **I**, **IV** and **V** benefit from significant stabilisation due to delocalisation of the nitrogen lone pair(s) into the vacant p-orbital at the arsenic centre. Although calculations indicate that the inherent π-donor capacity of phosphorus is similar to that of nitrogen,[11] P-As π-interactions should be disfavoured in diphosphaarsenium cations $[(R_2P)_2As]^+$, due to the high barrier to planarisation of phosphorus.

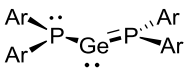


(**I**) (**III**)



(**II**) (**IV**)

We recently demonstrated that the appropriate choice of substituents enables the synthesis of diphosphagermylenes (**VI**, **VII**) which are stabilised by pπ-pπ interactions between a single planar phosphorus centre and the germanium atom.[12] Since compounds **VI** and **VII** are isoelectronic with the corresponding diphosphaarsenium cations, we speculated that a P-As π-stabilised diphosphaarsenium cation might be accessible. We detail below our attempts to prepare such a cation, its solid-state structure, its solution behaviour and an analysis of its bonding. In addition, we report the contrasting behaviour of a putative diphosphaphosphenium cation.



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ (**VI**)
2,4,6-*i*Pr$_3$C$_6$H$_2$ (**VII**)

The reaction between two equivalents of $[(Dipp)_2P]Na(THF)_{1.5}$[13] and $AsCl_3$ in cold THF yields the chloroarsane $\{(Dipp)_2P\}_2AsCl$ (**1**), along with a small quantity of the diphosphane $(Dipp)_2P\text{-}P(Dipp)_2$ and a very small amount of the secondary phosphane $(Dipp)_2PH$ [Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$] (Scheme 1). Storage of a solution of this material in a mixture of MeCN and Et_2O at -25 °C for 12 h leads to deposition of the co-

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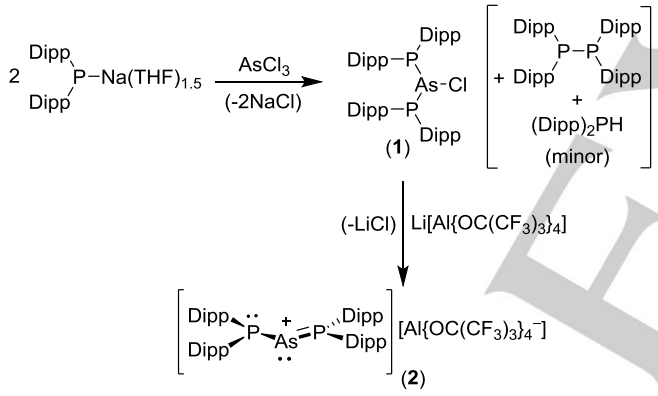
Supporting information for this article is given via a link at the end of the document. CCDC 1815449, 1815450, 1913170 and 1913171 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

crystals $\{(Dipp)_2P\}_2AsCl.(Dipp)_2P\text{-}P(Dipp)_2$ (**1a**, see Supporting Information). Subsequent removal of solvent from the supernatant gives **1** as a yellow powder in reasonable yield, although the product remains contaminated with a small amount of $Dipp_2PH$, which could not be removed.

Treatment of **1** with one equivalent of either $GaCl_3$ or $Na[BAr^F_4]$ in fluorobenzene gave deep green solutions, which, unexpectedly, exhibited no discernible peaks in their room temperature $^{31}P\{^1H\}$ NMR spectra, other than those due to small quantities of $(Dipp)_2PH$ and $(Dipp)_2P\text{-}P(Dipp)_2$ [Ar^F = C_6H_3-3,5-$(CF_3)_2$]. Although we were able to grow small green crystals of these supposed arsenium salts $[\{(Dipp)_2P\}_2As]^+[M]^-$ ($[M]^-$ = $GaCl_4^-$, $BAr^F_4^-$), these were not suitable for X-ray crystallography and so the identities of these compounds could not be verified. However, while the reaction between **1** and $Li[Al\{OC(CF_3)_3\}_4]$[14] in fluorobenzene initially gave a dark green oil on attempted crystallisation from a mixture of toluene and fluorobenzene, storage of this oil for approximately one week at -25 °C resulted in gradual crystallisation of the material. An X-ray crystallographic study of the resulting dark green crystals confirmed these to be of the diphosphaarsenium salt $[\{(Dipp)_2P\}_2As][Al\{OC(CF_3)_3\}_4].1½PhMe$ (**2**). Compound **2** decomposes only very slowly in solution at room temperature and is stable in the solid state for long periods.



Scheme 1. Synthesis of **1** and **2**.

Compound **2** crystallises with two crystallographically independent cation/anion pairs in the asymmetric unit, along with three molecules of toluene (Figure 1), all of which are disordered; the cations and anions are well separated (closest As…F contact >5 Å).

The two independent cations in **2** are subject to different modes of disorder: cation 1 (**2^1**) exhibits disorder of the arsenic atom and one phosphorus centre, along with its associated substituents, over two positions, while cation 2 (**2^2**) exhibits disorder of the two phosphorus atoms and the arsenic centre over two positions (see the Supporting Information). In each cation, the major disorder components (**2$^1_{maj}$** and **2$^2_{maj}$**, with 94 and 92% occupancy, respectively) possess one planar and one pyramidal phosphorus centre [sum of angles at P(1A) = 359.75, P(2A) = 320.16, P(3A) = 359.87, P(4A) = 319.49°]. The distances between the planar phosphorus centres and the arsenic atoms in **2$^1_{maj}$** and **2$^2_{maj}$** [2.1501(9) and 2.1482(9) Å, respectively] are approximately 6% (ca. 0.15 Å) shorter than the distances between the pyramidal phosphorus centres and the arsenic atoms [2.2925(7) and 2.3028(11) Å for **2$^1_{maj}$** and **2$^2_{maj}$**, respectively], suggesting a significant degree of multiple bond character in the former bonds. The short P-As distances in **2$^1_{maj}$** and **2$^2_{maj}$** are at the longer end of the range of P=As distances in the few crystallographically characterised phosphaarsenes RP=AsR, in which there is a true P=As double bond; for example, the P-As distances in (Mes*)P=As{$CH(SiMe_3)_2$} and (2,6-$Trip_2C_6H_3$)As=P(Mes) are 2.125(1) and 2.134(2) Å, respectively [Mes = 2,4,6-$Me_3C_6H_2$, Mes* = 2,4,6-*t*$Bu_3C_6H_2$, Trip = 2,4,6-*i*$Pr_3C_6H_2$].[15,16] However, the As-P(planar) distances in **2$^1_{maj}$** and **2$^2_{maj}$** are similar to the As-P distances in the 1,3-diphospha-2-arsaallyl *anion* in $(Mes^*P)_2AsLi(TMEDA)(Me_2NH)$ (**3**), recently reported by Wright and co-workers [As-P 2.176(1) and 2.170(1) Å; TMEDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine].[17] The P-As-P angles in **2$^1_{maj}$** and **2$^2_{maj}$** are 105.45(3) and 109.95(4)°. Overall, the structures of the cations **2$^1_{maj}$** and **2$^2_{maj}$** are remarkably similar to that of the isoelectronic diphosphagermylene **VI** [sum of angles at P = 358.35 and 311.53°, P-Ge-P angle 107.4(4)°].[12]

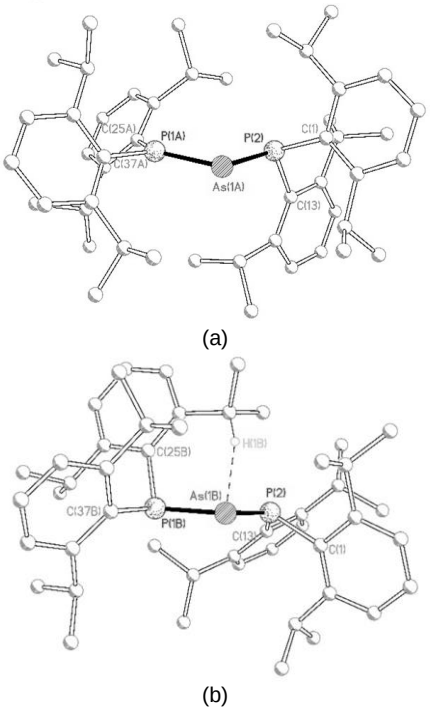


Figure 1. Solid-state structures of (a) the major (**2$^1_{maj}$**) and (b) the minor (**2$^1_{min}$**) disorder component of independent cation 1 of **2** with H atoms (except one methine H atom) omitted for clarity. Selected bond lengths (Å) and angles (°) for **2$^1_{maj}$**: P(1A)-As(1A) 2.1501(9), P(2)-As(1A) 2.2925(7), P(1A)-C(25A) 1.834(3), P(1A)-C(37A) 1.809(3), P(2)-C(1) 1.849(3), P(2)-C(13) 1.845(3), P(1A)-As(1A)-P(2) 105.45(3), As(1A)-P(1A)-C(25A) 135.75(11), As(1A)-P(1A)-C(37A) 111.28(10), C(25A)-P(1A)-C(37A) 112.72(14), As(1A)-P(2)-C(1) 95.72(8), As(1A)-P(2)-C(13) 118.30(10), C(1)-P(2)-C(13) 106.15(13). See main text for details of **2$^1_{min}$**.

The minor disorder components of the two independent cations (**2$^1_{min}$** and **2$^2_{min}$**) have rather low occupancies (6% and 8%, respectively), and so it is not appropriate to discuss their

structures in detail; however, the gross structural features of $\mathbf{2^1_{min}}$ and $\mathbf{2^2_{min}}$ are clear. Disorder component $\mathbf{2^2_{min}}$ adopts the same structural motif as $\mathbf{2^1_{maj}}$ and $\mathbf{2^2_{maj}}$, with one planar and one pyramidal phosphorus centre. In contrast, $\mathbf{2^1_{min}}$ adopts a structure with two pyramidal phosphorus centres [sum of angles at P(1B) = 324.5, P(2) = 339.97°]. Unexpectedly, this leads to a close approach of the methine hydrogen atom of one isopropyl group to the arsenic centre [H(1B)···As(1B) 2.02(1) Å], such that there appears to be an agostic-type C-H···As interaction (the agostic-type nature of this interaction is supported by DFT calculations, see below). We have previously reported related B-H···E agostic-type interactions (E = Sn, Pb) in phosphine-borane-stabilised dialkylstannylenes and –plumbylenes,[18] but, to the best of our knowledge, the C-H···As interaction in $\mathbf{2^1_{min}}$ is the first crystallographically observed C-H···E agostic-type interaction in a heavier main group carbene analogue.

The solvent of crystallisation in **2** is held only weakly; the ^{1}H NMR spectrum of a sample which had been subjected to vacuum for 10 mins is consistent with the alternative solvate $[\{(Dipp)_2P\}_2As][Al\{OC(CF_3)_3\}_4].½PhMe$ (**2a**). At room temperature the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **2a** in CD_2Cl_2 exhibit broad signals which are consistent with a single ligand environment. As the temperature is reduced the ^{1}H NMR spectra become increasingly broad, with overlapping signals which are difficult to interpret.

While at room temperature no signal is observed in the $^{31}P\{^1H\}$ NMR spectrum of **2a**, as the temperature is reduced, the spectrum resolves into three broad signals, **A**, **B** and **C** (Figure 2), which, at -20 °C, are in the approximate ratio 1:3:1. As the temperature is reduced further, signals **A** and **C** sharpen, while peak **B** sharpens and then broadens, although the approximate ratio of **A**:**B**:**C** remains 1:3:1. At -90 °C the spectrum consists of a pair of doublets at 223.9 (**A**) and -34.0 ppm (**C**, J_{PP} = 151.8 Hz), while the signal at 95.2 ppm (**B**) has broadened to such an extent that it is barely resolved, clearly suggesting further decoalescence of this peak. Unfortunately, we were unable to obtain a temperature low enough to observe this behaviour further. We were also unable to observe complete coalescence of the peaks at higher temperatures due to the instability of **2a** above ca. 40 °C.

The solid-state $^{31}P\{^1H\}$ CP-MAS NMR spectrum of **2a** exhibits two signals, a sharp singlet at -40.7 ppm with few spinning side bands and a broad signal at 217.4 ppm exhibiting a large degree of chemical shift anisotropy (see Supporting Information). These signals are clearly consistent with peaks **A** and **C** in the low temperature solution state $^{31}P\{^1H\}$ NMR spectrum. On the basis of their chemical shifts and the large chemical shift anisotropy of the low field signal in the solid-state spectrum, we attribute peaks **A** and **C** to the planar and pyramidal phosphorus centres in **2a**, respectively (for **2** DFT calculations suggest chemical shifts of 219 and 19 ppm for the planar and pyramidal phosphorus centres, respectively). For comparison, the chemical shifts of the two-coordinate phosphorus centres in phosphaarsenes typically lie in the range 530-670 ppm;[15,16] the chemical shift observed for the planar phosphorus centre in **2a** is closer to that observed for the 1,3-diphospha-2-arsaallyl anion in **3** (235.3 ppm for the *E*,*E*-isomer).[17]

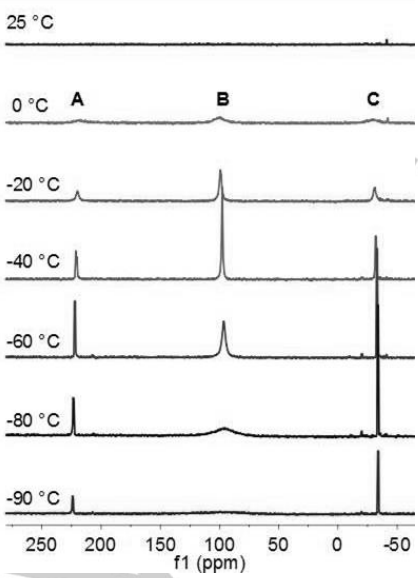
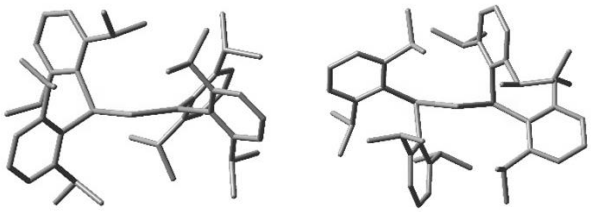


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **2a** in CD_2Cl_2.

The identity of the species responsible for peak **B** is less clear. We have previously observed similar variable-temperature NMR behaviour for the isoelectronic germylene **VI**: at -95 °C the $^{31}P\{^1H\}$ NMR spectrum of **VI** consists of a pair of broad signals at 98.5 and -82.0 ppm, corresponding to the planar and pyramidal phosphorus centres, respectively, along with two sharp singlets at 7.8 and -43.1 ppm, which we assigned to configurations containing two pyramidal phosphorus centres.[12] It is therefore likely that the low-temperature broadening of peak **B** is due to decoalescence into two peaks arising from configurations of **2a** with two pyramidal phosphorus centres. Consistent with this, DFT calculations suggest that an alternative configuration of **2**, with two pyramidal phosphorus centres, would give rise to a signal at 34 ppm.

In order to investigate the bonding in **2** we have carried out a DFT study. Local minima were found for configurations with one planar and one pyramidal phosphorus centre ($\mathbf{2_{plan}}$), corresponding to the solid-state structure of $\mathbf{2^1_{maj}}$, and with two pyramidal phosphorus centres ($\mathbf{2_{pyr}}$) (Figure 3). Attempts to locate a minimum corresponding to $\mathbf{2^1_{min}}$ were unsuccessful, each time converging to a geometry corresponding to $\mathbf{2^1_{maj}}$. Geometry $\mathbf{2_{plan}}$ is 25.7 kJ mol^{-1} lower in free energy than $\mathbf{2_{pyr}}$.

The calculated geometry of $\mathbf{2_{plan}}$ is very similar to the solid state structures of $\mathbf{2^1_{maj}}$ and $\mathbf{2^2_{maj}}$ [P-As-P angle 105.748°, P-As distances 2.1765 and 2.3003 Å]. Inspection of the molecular orbitals reveals that the P-As π-orbital is the HOMO-5, although this orbital also has large components on the aromatic rings, while the P-As π*-orbital is the LUMO (see the Supporting Information). NBO analysis yields Wiberg bond indices of 1.558 and 1.055 for the As-P(planar) and As-P(pyramidal) bonds, respectively, clearly indicating significant multiple bond character in the former. For $\mathbf{2_{pyr}}$, which exhibits no As-P multiple bond character, the Wiberg bond indices are both 0.936.



(**2**$_{plan}$) (**2**$_{pyr}$)

Figure 3. Minimum energy geometries of **2**$_{plan}$ and **2**$_{pyr}$ (B97D/6-311G(2d,p)).

In addition to the P=As π interaction, NBO analysis reveals that **2**$_{plan}$ is further stabilised by delocalisation of the arsenic lone pair into a P-C σ*-orbital associated with the planar phosphorus centre. Second order perturbation theory analysis indicates that the approximate stabilisation afforded by this interaction [the E(2) energy] is 45 kJ mol^{-1}. The stabilisation of **2**$_{plan}$ may therefore be characterised as an unusual version of the *push-pull* type, with the *push* arising from π-donation of the lone pair of the planar phosphorus atom into the vacant p-orbital at arsenic and the *pull* arising from delocalisation of the arsenic lone pair into a P-C σ*-orbital at the planar phosphorus centre.

In **2**$_{pyr}$ two of the aromatic rings are significantly canted towards the arsenic atom, such that the C_{ipso}···As distances are 2.4801 Å. This lies well within the sum of the van der Waal's radii of C and As (3.55 Å)[19] and suggests a significant bonding interaction between these atoms. Consistent with this, NBO analysis of **2**$_{pyr}$ reveals significant delocalisation of electron density from the aromatic rings into the formally vacant p orbital of the arsenic centre, such that the latter orbital has an occupancy of 0.53 electrons and the As···C_{ipso} Wiberg bond indices are 0.267; these interactions are calculated to stabilise **2**$_{pyr}$ by 208 kJ mol^{-1}. These arene···As interactions are related to the arene···E interactions in Menshutkin complexes such as $SbCl_3.C_6H_6$.[20,21] Complexes with arene···As interactions are much less common than similar complexes with Sb or Bi and there has been some debate as to the exact nature of these interactions;[20a,22] however, recent calculations suggest that, for arsenic-containing systems, they are best described as arising from donation of the arene π-electron density to the Lewis acid arsenic centre.[23] Nonetheless, in Menshutkin complexes, the interaction energies are calculated to be rather low (e.g. for $AsCl_3$···C_6H_6 the interaction energy is calculated to be just 27.1 kJ mol^{-1}),[22] suggesting a significantly weaker interaction than the C_{ipso}···As interaction in **2**$_{pyr}$. The strength of the calculated interaction in **2**$_{pyr}$ may be attributed to the more efficient overlap of the aromatic π-orbital and the vacant *p*-orbital in **2**$_{pyr}$ compared to the overlap of the aromatic π-orbital and the As-X σ*-orbitals in Menshutkin complexes.

Although we were unable to locate a stable minimum corresponding to the minor disorder component **2**$^{1}_{min}$, in order to probe the potential C-H···As agostic-type interaction a single point energy calculation was performed on the geometry corresponding to the crystal structure atomic coordinates (**2**$_{alt}$). NBO analysis suggests that, although both P centres have a somewhat pyramidal geometry in this structure, there remains a substantial P-As π-interaction from the P atom which is closer to planar. NBO analysis also suggests that there is a genuine C-H···As agostic-type interaction, with significant delocalisation of electron density from the C-H σ-bond into the P-As π*-orbital; this stabilises **2**$_{alt}$ by approximately 21 kJ mol^{-1}.

Given the unusual structure and solution behaviour of **2**, we became interested in preparing the analogous phosphenium cation $[\{(Dipp)_2P\}_2P]^+$. However, the reaction between two equivalents of $[(Dipp)_2P]Na(THF)_{1.5}$ and PCl_3 in cold THF gave a complex mixture of products, as judged by $^{31}P\{^1H\}$ NMR spectroscopy; this is likely due to the bulky nature of the Dipp substituents. In order to overcome this problem, we targeted the less hindered $\{(Mes)_2P\}_2PCl$ (**4**), which was successfully prepared by the reaction of two equivalents of $(Mes)_2PLi$ with PCl_3 in cold diethyl ether.

Treatment of a solution of **4** in fluorobenzene with $GaCl_3$ or $Li[Al\{OC(CF_3)_3\}_4]$ gave dark purple solutions, which quickly faded to pale yellow. Unfortunately, these reactions yielded only impure, pale yellow oils, which proved difficult to characterize. Similarly, the reaction between **4** and $Na[BAr^F_4]$ in fluorobenzene initially gave a dark purple solution, which again faded to pale yellow over the course of two mins. A $^{31}P\{^1H\}$ NMR spectrum of the crude reaction solution indicated the formation of a single product which gave rise to a doublet at 97.7 ppm and a triplet at -46.2 ppm (J_{PP} = 312 Hz), suggesting that a P_2P' unit persists in this compound. Single crystals were obtained from a PhF solution layered with methylcyclohexane and were shown by X-ray crystallography to be the unexpected diphosphinophosphonium salt [*cyclo*-$\{(Mes)P\}_2P(Mes)_2][BAr^F_4].C_6H_{11}Me$ (**5.CyMe**, Figure 4).[24]

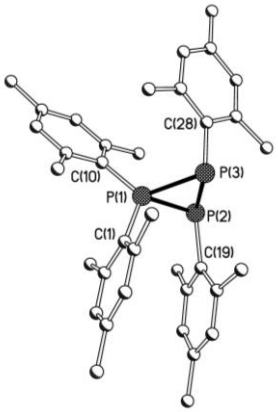
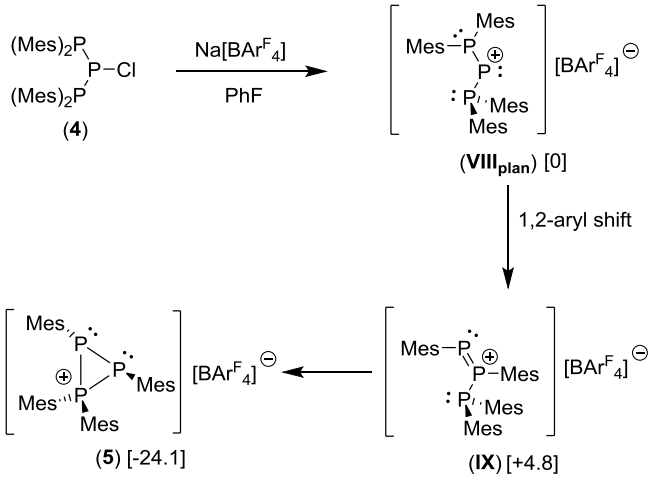


Figure 4. Solid-state structure of the cation of **5.CyMe**, with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-P(2) 2.2048(11), P(1)-P(3) 2.1984(10), P(2)-P(3) 2.2645(11), P(1)-C(1) 1.798(3), P(1)-C(10) 1.807(3), P(2)-C(19) 1.834(3), P(3)-C(28) 1.845(3), P(1)-P(2)-P(3) 58.91(3), P(1)-P(3)-P(2) 59.19(3), P(2)-P(1)-P(3) 61.90(4).

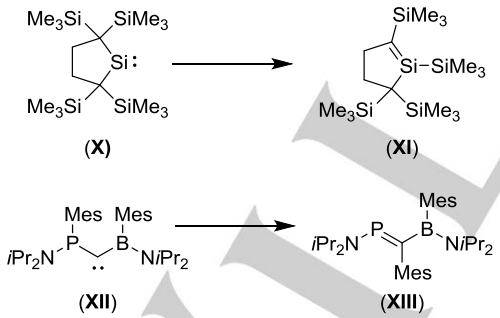
A similar structural motif has been reported by Burford and co-workers for a small series of diphosphinophosphonium cations, which were prepared by the quaternisation of cyclic triphosphines $(RP)_3$ with MeOTf.[25] In the present case, we propose that the initial reaction between **4** and $Na[BAr^F_4]$ yields the desired phosphenium salt (**VIII**), as evidenced by the dark purple colour of the solutions, which we suggest arises from *n*-π*/π-π* transitions in a diphosphaphosphenium cation possessing a

planar terminal phosphorus atom. This cation undergoes a 1,2-aryl shift to give the corresponding phosphine-substituted diphosphene cation (**IX**), which rapidly cyclises to give **5** (Scheme 2). Attempts to observe the intermediates **VIII** and/or **IX** by low temperature $^{31}P\{^{1}H\}$ NMR spectroscopy were unsuccessful.



Scheme 2. Proposed pathway to **5** [calculated relative free energies (kJ mol^{-1}) in square brackets].

In support of this mechanism, DFT calculations indicate that the cationic diphosphene **IX** is essentially isoergonic with the putative diphosphaphosphenium salt **VIII$_{plan}$** and that this latter compound is 28.9 kJ mol^{-1} higher in free energy than the cyclic cation **5** (see Supporting Information). Similar room-temperature 1,2-migrations to that proposed have been observed in closely related compounds; for example, the cyclic silylene **X** undergoes a 1,2-silyl migration to give the silene **XI**,[26] while the (boryl)phosphacarbene **XII** undergoes a 1,2-aryl migration to give the phosphaalkene **XIII** (Scheme 3).[27]



Scheme 3. Related 1,2-migrations of a silylene and a carbene.

In summary, we report a rare and unusually stable acyclic arsenium cation (**2**), the first example of such a cation to have two phosphorus substituents. This compound possesses one planar and one pyramidal P atom in the solid state, leading to substantial stabilisation through a P-As π-interaction. Attempts to prepare a diphosphaphosphenium analogue of **2** led to the isolation of a cyclic diphosphinophosphonium salt (**5**) via a 1,2-aryl migration/cyclisation process.

Acknowledgements

This work was partly funded by the U.K. Engineering and Physical Sciences Research Council (EPSRC; Grant EP/L5048281). The authors are grateful to Dr N. Rees (Oxford, UK) for obtaining the solid-state NMR spectra.

Keywords: arsenic • P-ligands • solid-state structure • density functional calculations • pi-interactions

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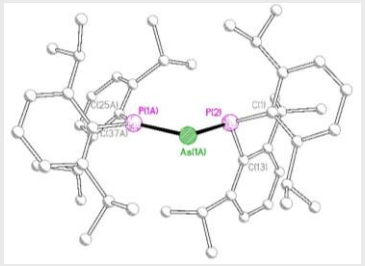
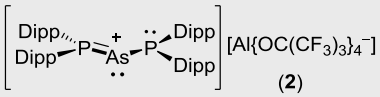
COMMUNICATION

The first diphosphaarsenium cation has been synthesised. This cation exhibits remarkable stability due to the delocalisation of a lone pair from a planar phosphorus centre into the vacant arsenic p-orbital.





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